# TITANIUM DIOXIDE FILM SYNTHESIZING METHOD AND THE PRODUCT THEREOF

## BACKGROUND OF THE INVENTION

### 1. Field of the Invention

The present invention relates to the synthesis of thin films on substrates and, more particularly, to a titanium dioxide film synthesizing method to synthesize nano-structured anatase titanium dioxide films on homogeneous or heterogeneous substrates.

### 2. Description of the Related Art

Nano-structured titanium dioxides have many applications owing to their superior photocatalytic, biocompatible, and many other properties. Conventional electrochemical anodic oxidation for synthesis of titanium dioxides uses bulk titanium as a substrate, which has limited application. There is known another titanium dioxide synthesizing method that directly immersing bulk titanium in highly alkaline solutions (for example, 5M NaOH), forming porous titanium dioxide films. Porous titanium dioxide films made according to this method often exhibit a mixed phase, such as $Na_2Ti_5O_{11}$+$TiO_2$ (rutile), or $TiO_2$ (rutile + anatase). Moreover, the pore size is usually in the micron range. This titanium dioxides synthesizing method is time-consuming because bulk titanium must be immersed in highly alkaline solutions for at least several hours.

Anatase $TiO_2$ has excellent photocatalytic characteristics. However, for application of anatase $TiO_2$ there are technical problems to be settled, more particularly the problem of how to join firmly the titanium dioxides and the substrates.

Conventional obtaining satisfactory adhesion between anatase titanium dioxides and substrates is still not an easy task. Further, because anatase titanium dioxides are photocatalytic, substrates made of organic materials tend to be decomposed by the titanium dioxides due to photocatalytic reactions. This is another problem to be conquered.

Therefore, it is desirable to provide a method of synthesizing titanium dioxide films on substrates that eliminates the aforesaid problems.

## SUMMARY OF THE INVENTION

The present invention has been accomplished under the circumstances in view. It is one object of the present invention to provide a titanium dioxide film synthesizing method, which synthesizes nano-structured titanium dioxide films with single anatase phase on substrates rapidly at room temperature. It is another object of the present invention to provide a titanium dioxide film synthesizing method, which is practical to synthesize titanium dioxide films on homogeneous substrates as well as heterogeneous substrates. It is still another object of the present invention to provide a titanium dioxide film synthesizing method, which is practical to synthesize titanium films of uniform properties. It is still another object of the present invention to provide a titanium dioxide films synthesizing method, which enables synthesized titanium dioxide films to be firmly adhered to substrates. It is still another object of the present invention to provide a nano-structured titanium dioxide film.

To achieve these and other objects of the present invention, the titanium dioxide film synthesizing method, comprises the step of coating a titanium film on the surface of a substrate, and the step of using the titanium-coated substrate or the step of using a bulk titanium substrate as anode in an electrolyte to synthesize an anatase titanium dioxide film on the surface of the titanium by employing electrochemical

anodic oxidation. The titanium dioxide film has a nano-granular structure or a nano-network structure.

## BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a microscopic picture obtained from the surface of a finished product made according to the first embodiment of the present invention.

FIG. 2 is a microscopic picture obtained from the cross section of the finished product made according to the first embodiment of the present invention.

FIG. 3 illustrates the Raman spectra of the finished product made according to the first embodiment of the present invention.

FIG. 4 is a microscopic picture obtained from the surface of the finished product made according to the first embodiment of the present invention after heated at 500°C for 2 hours.

FIG. 5 illustrates the Raman spectra of the products made at different stages according to the first embodiment of the present invention.

FIG. 6 is a microscopic picture obtained from the surface of a finished product made according to a second embodiment of the present invention.

FIG. 7 illustrates the Raman spectra of the products made at different stages according to the second embodiment of the present invention.

## DETAILED DESCRIPTION OF THE INVENTION

The first embodiment of the present invention is to synthesize titanium dioxide films on a homogenous substrate (titanium) or heterogeneous substrate (silicon or any of a variety of semiconductors, metal, glass, ceramics, or polymers). For illustration only, the first embodiment is described to synthesize titanium dioxide films on a silicon substrate.

The method of the first embodiment of the present invention includes two

stages, namely, the first stage of pre-deposition and the second stage of electrochemical anodic oxidation. The first stage of pre-deposition is to deposit a titanium film on a silicon wafer by sputtering. Titanium film can also be deposited on a bulk titanium or substrate of any of a variety of other materials. The second stage of electrochemical anodic oxidation is to synthesize a nano-network structured titanium dioxide film on the titanium-coated silicon wafer in highly alkaline electrolytes, such as KOH (potassium hydroxide). In other words, the invention is to form a titanium seeding layer on a substrate, and then use this titanium seeding layer as a base to form a titanium dioxide film thereon by electrochemical anodic oxidation.

The method of the first embodiment of the present invention is described in detail by way of an example as outlined hereinafter with reference to FIGS. 1 and 2. At first, coat a titanium film **12** on the surface of a silicon wafer **10**. The titanium film **12** is deposited on a 4 inches P-type (100) silicon wafer **10** (of resistance over 4~7 Ωcm) by unbalanced magnetron sputtering. The deposition parameters are: target current: 0.9 A; working pressure: 1 mtorr; background pressure: $8 \times 10^{-6}$ torr; bias voltage: -50V; substrate temperature: 25°C; deposition time: 80 seconds; thickness of deposited film: about 0.5 μm. Evaporation is another way to do the same work.

Thereafter, put the titanium film **12**-coated silicon wafer **10** in electrolytes wherein the titanium film **12** is used as anode electrode, and 1M KOH solution is used as electrolytes, and then synthesize an anatase phase titanium dioxide film **14** on the surface of the titanium film **12** by electrochemical anodic oxidation at room temperature wherein the working electrode area is fixed at about $1 cm^2$; Pt (platinum) is used as cathode; the distance between anode and cathode is 11 cm; reference electrode is Ag/AgCl adapted to measure surface voltage of anode; the distance between the tip of reference electrode and anode is 3 mm; the electrochemical system is a bipolar

system; power supply voltage ranges from 0~100 V; power supply current ranges from 0~1 A; deposition mode can be a scanning electrolytic voltage mode or a potentiodynamic mode.

Field-emission SEM results show that a nano-network structured titanium dioxides film **14** was found on the titanium film **12** within about 5 minutes with scanning from 0 V to a cutoff voltage of 3 V in the rate of 10 mV/s. The nano-network structured titanium dioxides film **14** has a surface appearance as shown in FIG. 1 within about 17 minutes when scanning cutoff voltage at 10 V. The obtained network structure is uniform. The inner diameter of the network rings is about 50 nm and the ring width is less than 10 nm. The cross section of the titanium dioxides film **14** is as shown in FIG. 2. The thickness of the titanium dioxides film **14** is 60 nm. This titanium dioxide, titanium and substrate are attached to each other firmly. Therefore, this method effectively solves the adhesion problem between titanium dioxide photocatalyst and substrate. When the scanning voltage increased to 70 V, the thickness of the titanium dioxides film **14** could reach as high as 250 nm.

Raman spectroscopy shows the crystal structure of the titanium dioxide as indicated in FIG. 3, wherein **p** curve, **q** curve, and **r** curve are the Raman spectra of the titanium dioxide films **14** produced by using the scanning electrolytic voltage mode (scanning rate at 10 mV/s) when scanned to 10 V, 20 V, and 30 V. These three scanning conditions commonly show that titanium dioxide with single anatase phase was successfully synthesized. In FIG. 3, **s** curve is the Raman spectrum of the titanium-coated silicon wafer before anodic oxidation for contrast.

FIG. 4 shows the surface structure of the titanium dioxide after annealing at 500°C under atmospheric pressure with temperature ramping rate of 5°C per minute and temperature soaking time at 2 hours. As indicated, the nano-network structure

sustains. Raman spectroscopy shows that the obtained anatase phase under this temperature fully transformed to a rutile phase as shown in FIG. 5, wherein **a** curve was obtained from a titanium-coated silicon wafer without anodic oxidation; **b** curve was obtained from an anatase phase titanium dioxides film on a titanium-coated silicon wafer through anodic oxidation; **c** curve was obtained from a rutile phase titanium dioxide after annealing at 500°C under atmospheric pressure. The nano-network structure could sustain to at least 600°C, having enormous potential biocompatible applications.

During actual practice, the parameters for the second stage may be changed subject to actual requirements to achieve expected results. For example, electrolyte containing alkaline metal ions, for example, NaOH (sodium hydroxide) electrolyte may be used to substitute for KOH electrolyte. Electrolyte concentration could be ranged from 0.1~10 M. The concentration of KOH electrolyte is preferably at 1M. Voltage scanning rate could be within 0 mV/s~200mV/s. Scanning cutoff voltage could be ranging from 3 V to 85 V. Electrochemical anodic oxidation duration could be ranging from 5 minutes to 10 hours. The operation temperature is preferably within about 15°C~90°C. Nano-network structured anatase phase titanium dioxide can also be obtained by using a potentiodynamic mode ranging from 30 to 70V. Besides, if the substrate is bulk Ti, the first stage could be eliminated. The uniform nano-network structured $TiO_2$ film can be directly formed on the surface of bulk Ti as described above for the second stage.

Further, similar result can be obtained by using highly acid solution, for example, sulfuric acid as electrolyte. FIG. 6 is microscopic picture obtained from the surface of a titanium dioxide film on a titanium-coated silicon wafer made by using anodic oxidation with scanning electrolytic voltage mode (scanning rate 10 mV/s)

performed in 1M $H_2SO_4$ electrolyte at room temperature when scanned to 60 V. As shown in the picture, the titanium dioxide has a granular structure with uniform surface property. The diameter of the grains is about 10 nm, of nanometer structure. Raman spectroscopy shows the result as indicated in FIG. 7, wherein **e** curve, **f** curve, **g** curve, **h** curve, and **i** curve are spectra of titanium dioxide films respectively produced by using scanning rate at 10 mV/s when scanned to 7 V, 10 V, 20 V, 30 V, and 60 V (scanning cutoff voltages) respectively. Except **e** curve, all show that single anatase titanium dioxide was successfully synthesized, i.e., a single anatase titanium dioxide crystallized structure could be produced when scanning cutoff voltage is over 10V.

The method of the present invention enables nano-structured titanium dioxide to be synthesized within only several minutes on different substrates, especially heterogeneous substrates at room temperature. In application, the nano-structured anatase titanium dioxide film has optimum photocatalytic characteristics. This titanium dioxide/titanium/substrate structure could protect the substrates from photocatalytic decomposition, showing significant improvement on conventional techniques. Because a titanium dioxide structure made according to the present invention is nano-network structured which inner diameter can be adjusted from 1~200 nm subject to practical requirement, it has enormous potential solar battery (anatase phase) and biomedical (rutile phase) applications.